

THE STRUCTURE OF BITUMENS: CHARGE-TRANSFER NATURE

Teh Fu Yen

University of Southern California
2025 Zonal Avenue
Los Angeles, California 90033

Introduction

Most recently, we have been able to use the technique of electron spin resonance (ESR) (1,2) to elucidate the structure of native bitumens and have been able to reclassify the natural bitumens according to the differences in structure. The present work represents a portion of the continuous effort toward the correlation of structural features with the chemical and physical properties of these naturally occurring macromolecules.

X-ray diffraction (3,4), graphic densimetric methods (5,6), mass spectrometry (7,8,9), and ESR (9,10,11) have been used to show that naturally occurring bitumens contain large, fused-ring aromatic systems associated in stacked arrays. Generally, these aromatic systems consist of 2-dimensional disc-like planes, having a layer diameter ranging from 8.5-15.0 Å. These measurements correspond to the sizes of peri-condensed polynuclear aromatic hydrocarbons (PAH) of approximately 7-18 ring systems. Carbon chains assuming a zig-zag configuration are substituted on the edges of these individual planar discs in such a manner as to resemble those of paracyclophane molecules. These discs are associated in crystallites consisting of 5 or 6 layers in a stack with interlayer distances varying from 3.4-3.7 Å. These graphite-like crystallites are randomly distributed (although oriented) over a continuous mesomorphic media which contains both naphthenic and aliphatic structures (4,7).

Most of the molecules in the asphaltene fractions of bitumens are alkyl-substituted polycarbocyclic hydrocarbons (13). As to the resin or maltene fraction, most of its molecules contain heterocyclic systems and exhibit polarity due to functional substituents (8,14). Among the most frequently occurring and typical of these heteroaromatics is the petroporphyrin (15), an 18-diaza-annulene system (4). Hence, bitumens can be considered as being composed of polycyclic aromatic compounds bearing different functional groups. These individual components possess varying degrees of charge-transfer ability depending upon their relative donor or acceptor abilities.

For asphaltics, it has been possible to intercalate (16) a known acceptor such as iodine between the layers of alkyl-substituted polyaromatic systems which behave as donors. Experimentally, the interlayer distance of an iodine asphaltic complex increases from 3.5 Å to 8.7 Å, corresponding to the separation formed from the insertion of an axially intercalated iodine molecule (4x1.33 Å). Other evidence supporting this observation includes the occurrence of the 1080 cm^{-1} infrared donor-acceptor band, the increase in spin concentration of the iodine asphaltic complex and lowering of resistivity and gap energy in electrical measurements.

Up to the present, little work on the charge-transfer properties of bitumens has been published. This investigation represents the first reported experimental attempt at using infrared methods to study the charge-transfer characteristics of the polyaromatic molecules and to reveal the nature of their association within the bitumens.

Experimental

The asphaltene and resin fractions of bitumens were prepared by the conventional pentane/propane precipitation method described in an earlier paper (3).

The donor-acceptor complexes were made by dissolving the donor and the acceptor in boiling benzene; the molar ratio of acceptor to donor was, in all cases, 1 or slightly greater than 1. The reaction mixture was allowed to stand at room temperature for 24-48 hours to permit the separation of a solid. The product was then isolated, thoroughly washed with benzene and its melting point determined and checked with a literature value when available. The spectra were obtained with a Beckman IR-12 double beam instrument. For solid phase measurements, films, Nujol mulls, and potassium bromide pellets were prepared in the conventional fashion. Sets of matched cells of fixed thicknesses were used, for solution determinations, and, at the concentrations employed (0.50-0.25 g/ml), measurements were consistent with Beer's Law. High or intermediate resolution settings were used for scanning. The estimated error in the wavenumber based on repeated scans was $\pm 1 \text{ cm}^{-1}$.

Results

When bitumens are examined in the $1,000-625 \text{ cm}^{-1}$ region ($10-16\mu$), four bands located at approximately 865, 815, 760, and 730 cm^{-1} are observed. Examples of such spectra are shown in Fig. 1 and are represented by a visbreaker tar, two asphaltene fractions, and one resin fraction. These observations are generally unique to the naturally occurring or altered bitumens (17). The first three bands correspond closely to those for aromatic C-H out-of-plane bending vibrations (isolated, 2- and 3-adjacent C-H bonds), whereas the fourth band, occurring at a shoulder at $731-720 \text{ cm}^{-1}$, appears to be due to in-plane methylene rocking vibrations (18) of paraffinic nature.

Table I

OBSERVED SHIFT OF FREQUENCIES OF BENDING VIBRATIONS FROM A WEST TEXAS ASPHALTIC IN VARIOUS MEDIA

<u>Media</u>	<u>Number of Bands</u>				<u>ϵ</u>	<u>$(\epsilon-1)/(2\epsilon+1)$</u>
	<u>(cm^{-1})</u>					
	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>		
Film	874	816	753	724		
n-Hexane	873	815	752	---*	1.925	0.19
Carbon disulfide	873	816	755	725	2.641	0.26
1-Iododecane	876	816	---	---	3.93**	0.33
Chloroform	881	---	---	---	4.806	0.36
n-Heptyl acetate	---	---	767	---	4.81**	0.36
Methyl iodide	---	---	760	---	7	0.40
Benzonitrile	880	823	---	---	25.58	0.49

*Dashed line represents dead regions.

**Approximated values from homologous series.

The results summarized in Table I show the effect of the dielectric constant of solvents on the positions of the four bands as compared with the reference spectrum for the solid phase (without solvent) for a bitumen resin fraction. The sample was differentially scanned in the presence of seven solvents of varying degrees of polarity: n-hexane, carbon disulfide, 1-iododecane, chloroform, n-heptyl acetate, methyl iodide, and benzonitrile. When compared to the spectrum of a solid portion of this sample, shifts toward the blue were observed for the first three bands; these represent the aromatic C-H bending vibration (in this region,

there is no absorption by the solvents). No significant displacement was observed for the fourth band (methylene rocking). Spectra obtained in this manner were exemplified by 1-iododecane, as shown in Fig. 2. The shift of the first three bands becomes larger as the dielectric constant of the polar medium increases.

The extent of the shift becomes more striking when the sample is allowed to react with complexing reagents such as nitro- or cyano-bearing acceptors (picric acid, s-trinitrobenzene, p- or m-dinitrobenzene, tetracyanoethylene). Since the composite aromatic system in bitumens does not form well-defined complexes, a simple technique had to be devised for forming the donor-acceptor charge-transfer complex in situ. This was accomplished by adding the donor to an excess of the acceptor in a solvent and scanning the resulting solution against the pure acceptor in the same solvent. This procedure was tested with perylene and s-trinitrobenzene in a nitrobenzene-carbon disulfide solution and shown to yield peaks identical in position to those found with the Nujol mull scan of the solid complex of perylene-s-trinitrobenzene as shown in Fig. 3 (772 cm^{-1} instead of 773 cm^{-1} from the solid sample; 818 cm^{-1} instead of 821 cm^{-1} from the solid sample).

In this fashion, it was possible to obtain satisfactory spectra for different fractions of bitumens. Fig. 4 summarizes the results of these spectra for three different complexing media (5% tetracyanoethylene in benzonitrile; 2.5% s-trinitrobenzene in 1:10 nitrobenzene-carbon disulfide; 2.5% m-dinitrobenzene in 1:10 nitrobenzene-carbon disulfide) and one non-complexing solvent (methyl iodide). A similar shift pattern was also observed for a Wafra asphaltene in three different media (Fig. 5). The shifts were as anticipated, although, however, the bands became broader. The dashed line in Fig. 2 represents the "dead region" of the media (region of solvent absorption interferences).

Table II

					2.5% ³ s-TNB ₃ in NO ₂ ϕ- carbon disulfide (1:10)	2.5% ⁴ m-DNB ₄ in NO ₂ ϕ- carbon disulfide (1:10)	2.5% ⁵ p-DNB ₅ in NO ₂ ϕ- carbon disulfide (1:10)	2.5% ⁶ FA ₆ in NO ₂ ϕ- carbon disulfide (1:10)
<u>Sample</u>	<u>Band Number</u>	<u>Solid Matrix</u>	10% NO ₂ ϕ ¹ in carbon disulfide	5% TCE ² in benzo- nitrile				
West Texas Resin	(1) (2) (3) (4)	874 816 753 724	891 825 764 727	886 835 --- ---	885 822 762 726	890 828 867 ---	890 825 762 727	887 825 765 ---
Baxterville Resin	(1) (2) (3) (4)	870 812 750 725	--- --- --- ---	--- --- --- ---	885 824 766 ---	--- --- --- ---	--- --- --- ---	--- --- --- ---
Raudhatain Asphaltene	(1) (2) (3) (4)	866 817 757 732	869 823 765 730	--- --- --- ---	873 820 759 ---	--- --- --- ---	873 824 765 ---	--- --- --- ---

1. Nitrobenzene
2. Tetracyanoethylene
3. s-Trinitrobenzene
4. m-Dinitrobenzene
5. p-Dinitrobenzene
6. Picric acid

Fractions of other bitumens gave similar results as indicated in Table II. The displacement for the first three bands was 10-15 cm^{-1} , while that for the fourth band was only 2-3 cm^{-1} . The extent of the shift of aromatic C-H bending vibration bands is of the same order of magnitude as observed for those of pure PAH (18,19). One such example is provided by the perylene-s-trinitrobenzene complex as shown in Fig. 3. The C-H bending of perylene shifted toward the blue from 767 cm^{-1} (3- γ) to 733 cm^{-1} . On the other hand, the C-H bending of the acceptor, s-trinitrobenzene shifted toward the red from 922 cm^{-1} (1- γ) to 909 cm^{-1} .

Discussion

The polyaromatic systems within the bituminous structures undergo charge-transfer processes readily. In the presence of a known acceptor, the aromatic system usually behaves as a donor; this is due to the fact that asphaltic molecules bear numerous short alkyl chains such as methyl or ethyl groups (13), which are known to be electron releasing. Association due to the π - π overlap usually occurs when there is a charge-transfer from a π -donor to a π -acceptor. Charge-transfer may occur to varying degrees, the extreme case being the formation of two separate ions.

The frequency shift of an absorption band arising from a substance in solution can normally be predicted by the Kirkwood-Bauer-Magat (KEM) rule, which states that the shift, $-\Delta\mu/\mu$, proportional to $(n^2-1)/(2n^2+1)$, $(\epsilon-1)/(2\epsilon+1)$ where n is the refractive index and ϵ is the dielectric constant of the solvent. In this manner, a red shift is expected, since both n and ϵ are greater than unity. The KEM relation was based on the concept of non-localized interactions between a simple oscillating dipole (solute) and an electric field within a spherical cavity, in a continuous dielectric (solvent). On the other hand, Kienitz (20) and La Lau (21) have independently found that the aromatic C-H bending bands of aromatics in polar solvents are shifted in a direction opposite to that predicted by the KEM relation. They have explained their blue shift data on the basis of localized electrostatic interaction. The observations of the blue shifts reported in Table I are in agreement with those of Kienitz and La Lau and are also consistent with the results obtained from pure PAH investigations (18). Localized interactions in a given charge-transfer process, involving π - π systems, are to be anticipated.

Hence, the strong effect of the frequency shift in the case of complexing media in Fig. 2 can be explained on the basis of an even stronger localized interaction between the donor and acceptor molecules. The energy for the donor-acceptor charge-transfer process usually consists of the ionization potential of the donor and the electron affinity of the acceptor; in terms of the molecular orbital theory (MO), the energy may be expressed as the difference between that of the highest, filled MO of the donor and the lowest, filled MO of the acceptor. The blue shift for the donor and the red shift for the acceptor have been found for PAH (19). For a given acceptor, the frequency shifts of the donors are proportional to their molecular orbital m -values. Presumably, in a charge-transfer process which is associated with a partial removal of electrons from the bonding orbitals of the donor to the antibonding orbitals of the acceptor, the change in vertical energy not only affects the extinction coefficient of a vibrational band, but also influences the force constant of certain modes.

The polyaromatic systems in bitumens consist of alkyl-substituted polynuclear aromatics, π -deficient heteroaromatics, π -excessive heteroaromatics and, electro-negatively substituted aromatics, etc. The association of polyaromatics can be visualized as a close approach of two different aromatic systems; for example, π -deficient and π -excessive heteroaromatic molecules. It is yet possible that there are associations between molecules of the same type e.g., the fully alkyl-substituted aromatics and the less alkyl-substituted aromatics. This type of π - π association

is the cause of stack formation in bitumens as observed by x-ray diffraction, both in high angle (4) and in low angle (22) ranges.

In general, molecular interaction is favored by the close proximity of orderly packed rod- or disc-shaped molecules. For mononuclear homocyclic aromatics (benzenes), optimum interaction is achieved when the molecules are in stacked positions so that the charge clouds can be superimposed. The layer-like configuration of the aromatic moiety in paracyclophanes having short folding polymethylene bridges, and for isotactic polystyrenes is achieved through the interannular interactions of π -electrons such that the flexibility of the polymethylene chains is inhibited, e.g., 3_1 -helix.

Since porphyrins are present in the composites of bitumens (14), a study of the nature of metalloporphyrins occurring in bitumens (11,23,24,25) could probe the nature of association among various aromatic molecules within bitumens. By ESR methods, the temperature dependence of the anisotropy of the vanadium hyperfine structures in different polar media results in a dissociation energy of approximately 10-14 kcal (26). Similarly, dissociation energy of the vanadyl stretching mode is about 17 kcal (27). This order of dissociation energy is a measure of the extent of association of the porphyrin (free) with other polyaromatic systems (fixed or bound) in bitumens. Very recently, the observation of nitrogen superhyperfine structures of vanadium chelates in bitumens also suggest the presence of this type of association behavior (12). In order to separate vanadyl porphyrin from polyaromatic molecules in bitumens, both elevated temperature and a polar solvent are required (28,29).

Many colloidal characteristics of bitumens such as its gel-sol conversion, temperature coefficient of viscosity, complex flow, and micelle stability, etc. may be explained on the basis of the charge-transfer nature of individual aromatic systems throughout the macrostructure (30,31). Consequently, the inter- and intra-cluster associations not only affect processing, treatment, and refining, but are also relevant to the problems concerning pollution, recovery, geochemistry, and genesis of all bituminous materials (32).

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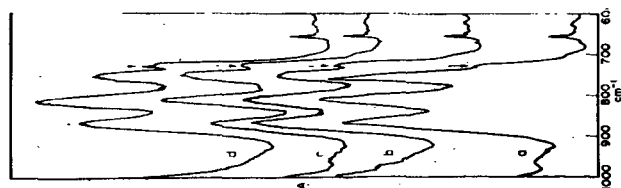


Fig. 1. Typical Bending and Rocking Vibrations of

Some Bitumens:

- a. Asphaltene from Kuwait Visbreaker Tar
 - b. Asphaltene from Mara Crude
 - c. Resin from Baxterville Crude
 - d. Asphaltene from Raudhatain Crude
- (Spectra for asphaltic sample in carbon disulfide vs. carbon disulfide, r is methylene rocking, numbers in parentheses are 1, isolated; 2, 2-adjacent; 3, 3-adjacent C-H bending).

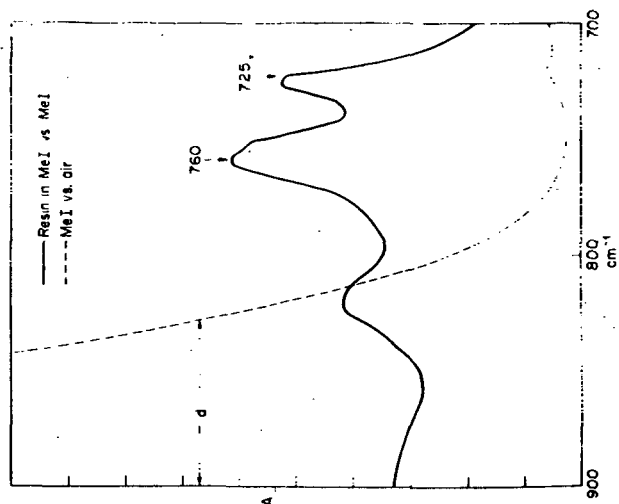


Fig. 2. Typical Infrared Differential Spectrum for a West Texas Resin in Methyl Iodide

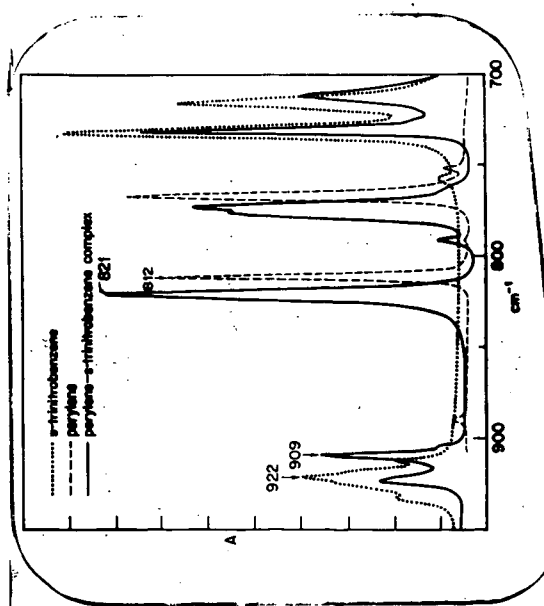


Fig. 3. Infrared Spectra of a Typical Donor-Acceptor Charge-Transfer Complex in the Bending Region (Nujol Mull)

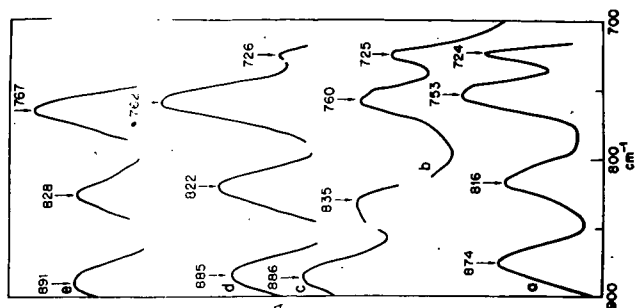


Fig. 4. Differential Infrared Spectra of a Resin Fraction from a West Texas Crude in Nujol

- a. Methyl Iodide
- b. 5% Tetracyanoethylene in Benzonitrile
- c. 2.5% s-Trinitrobenzene in Nitrobenzene
- d. 2.5% m-Dinitrobenzene in Nitrobenzene
- e. Carbon Disulfide (1:10)

(The discontinued line represents the "dead" region of the media)

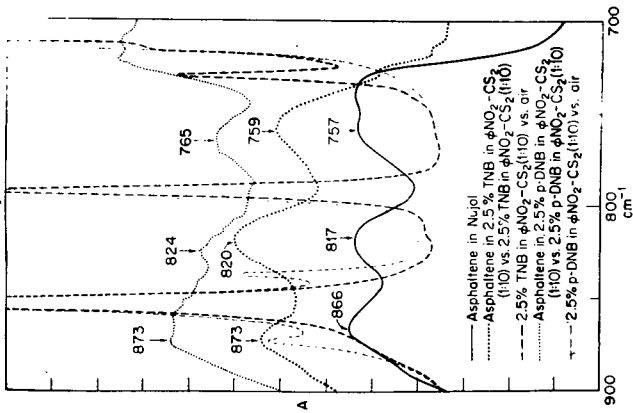


Fig. 5. Differential Infrared Spectra of the Asphaltene Fraction from a Wafra Heavy Residua in Different Complexing Media